buffer solutions) as titration was carried out with an aqueous solution of tetra-*n*-butylammonium hydroxide (Fischer Scientific Co., 0.40 ± 0.02 M). The pH at neutralization was 9.5 ($MeOH/H_2O$ (2/1) by volume), and at half-neutralization it was 5.72 (14/5 by volume). Rotary evaporation at water pump pressure gave a residue which was dried by addition of toluene (Burdick and Jackson, 150 mL) and further reduced-pressure evaporation. The resulting yellow solid was dissolved in ethyl acetate (200 mL), filtered, and cooled to -14 °C overnight. Yellow crystals were removed by suction filtration and allowed to dry in air (11.19 g, 91%, mp 110.5-112 °C). An analytical sample was prepared via a second recrystallization from ethyl acetate, followed by drying at 56 °C (0.2 torr for 24 h: mp 111.5-112 °C; NMR ($CDCl_3$) δ 0.95 (s), 1.05 (s), 1.2-1.8 (br m), 3.46 (s), 8.15 (s); IR (KBr) 2960, 1730, 1695, 1648, 1549, 1539, 1435, 1368, 1307, 1240, 1184, 1145, 1080 (vs), 969 cm^{-1}. Anal. Calcd for $C_{27}H_{49}NO_8$: C, 62.87; H, 9.60; N, 2.72. Found: C, 62.70; H, 9.55; N, 2.66.

Preparation of Salt 2b from 1a. Titration of **1a** (5.0 g, 0.0182 mol) in methanol (50 mL) and deionized water (13 mL) with aqueous sodium hydroxide (0.49 M) gave an equivalence point at pH 9.5 and a half-neutralization point at pH 5.6. At the equivalence point the methanol:water ratio was 1:1 by volume, and at the half-neutralization point the ratio was 5:3. Workup by rotary evaporation and recrystallization from methanol (hot filtration) gave sodium salt **2b** in 89% yield (4.80 g): mp 263-265 °C;[18] IR (KBr) 1680 (br), 1640 (br), 1545 (br), 1435, 1250, 1175 (br, vs), 1090 (br) cm^{-1}.

Pentamethyl 1-Butene-1,1,3,3,4-pentacarboxylate (3). This run represents the optimum of six trials, using various techniques. Methyl bromoacetate (1.13 g, 0.0067 mol) and acetonitrile (Burdick and Jackson, 150 mL) were added to a 250-mL round-bottomed flask which was connected to a Soxhlet apparatus. Sodium salt **2b** (2.0 g, 0.0067 mol) was added to the Soxhlet thimble, and the liquid was heated to reflux. After 1 day of reflux, all the salt had been extracted; heating was continued for a further 48 h, and the system was allowed to cool, furnishing a clear yellow solution with a white precipitate. Filtration (suction), and evaporation of the filtrate in vacuo, gave a dark orange residue which was extracted with anhydrous ether (12 mL) and the extract was concentrated in vacuo to give a second orange residue. Bulb-to-bulb distillation (130-150 °C oven temperature/10^{-3} torr) gave 2.20 g (94%) of pentamethyl ester **3** which crystallized on seeding: mp 59-60 °C; NMR (CCl_4) δ 3.12 (s), 3.51 (s), 3.58 (distorted s), 3.67 (s), 7.44 (s); IR (neat) 2990, 1740 (vs), 1378, 1348, 1240 (vs), 1100, 1080, 1132 (vs) cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_{10}$: C, 48.56; H, 5.24. Found: C, 48.80; H, 5.04.

Various other conditions were investigated for synthesis of this pentaester. Alkylation of the tetra-*n*-butylammonium salt **2a** in glyme or in acetonitrile with heating gave a product showing an impurity in the NMR spectrum at 1.5 ppm. Reaction of the same salt in acetonitrile at room temperature for 5-7 days, sometimes with 10-15% excess methyl bromoacetate, gave the ester **3** without the above impurity, but in lower yield. The sodium salt **2b** is so sparingly soluble in glyme that the Soxhlet extraction technique failed completely. Doubling the scale of operation in the detailed synthesis described above, but with 10% excess methyl bromoacetate, furnished the pentaester in 89% yield.

It was difficult to obtain the initial seeds of this new compound: the usual methods involving cooling and scratching proved ineffective. The first crystals appeared on concentration in vacuo of the carbon tetrachloride solution used for obtaining the NMR spectrum.

Attempted Michael Condensation on Ester 3. Preliminary studies with dimethyl malonate in methanol, employing catalytic amounts (ca. 5%) of sodium methoxide, indicated that molar amounts of base would be necessary in order for products to be isolated.

Sodium (0.069 g, 0.0029 mol) was added to methanol (Burdick and Jackson, 10 mL), and when the sodium had dissolved, dimethyl malonate (Aldrich, 1.91 g, 0.0145 mol, 400% excess) was added, followed by pentamethyl 1-butene-1,1,3,3,4-pentacarboxylate (1.0 g, 0.0029 mol). The mixture immediately became bright yellow-green and was allowed to stand at room temperature for 5 days. Evaporation of the methanol at water pump pressure gave a somewhat viscous orange-green residue, which upon evacuation at 10^{-3} torr (room temperature) yielded dimethyl malonate (1.39 g) in a trap cooled with dry ice/Dowanol. The remaining viscous yellow residue was extracted with methylene chloride and water, and upon evaporation of the organic phase from the dried extract, and bulb-to-bulb distillation of the resulting residue at 10^{-3} torr, two fractions were obtained: (1) bp 50-80 °C (0.35 g, 59%) and (2) bp 80-150 °C (0.2 g). NMR analysis and comparison with an authentic sample identified the main component of this neutral fraction as trimethyl ethane-1,1,2-tricarboxylate: NMR (CCl_4) δ 2.70 (d, J = 7 Hz), 3.52 (distorted s), 3.57 (distorted s). The yellow aqueous phase from the above workup was acidified with 6 M hydrochloric acid, whereupon it turned cloudy white. Extraction with methylene chloride (3 × 5 mL), drying ($MgSO_4$), and evaporation in vacuo gave 0.49 g (62%) of ester **1a**, identified by NMR analysis.

Preparation of Trimethyl Ethane-1,1,2-tricarboxylate (5). (With Mr. Ying Ki Kwong). Sodium hydride (3.53 g, 0.15 mol) was covered with glyme (100 mL) in a nitrogen-flushed 250-mL, round-bottomed flask, and the contents were stirred magnetically. Under ice cooling, dimethyl malonate (19.4 g, 0.15 mol) was slowly added. The mixture was allowed to warm to room temperature, and methyl bromoacetate (freshly distilled, 22.77 g, 0.15 mol) was added dropwise; an exothermic reaction occurred and a white precipitate formed. After addition of the methyl bromoacetate was complete, the mixture was stirred for 1 h at room temperature, followed by 1 h at reflux temperature. The cooled mixture reacted neutral to pH paper; it was filtered, the filtrate concentrated on a rotary evaporator at 20 torr, and the residue distilled at 0.02 torr. Three fractions were obtained: (1) bp 25-45 °C (positive sodium fusion test for bromine); (2) bp 81 °C, mp 31-32 °C[21] (14.9 g, 50% of the triester), and (3) bp 110 °C, consisting of the disubstitution product, tetramethyl propane-1,2,2,3-tetracarboxylate (identified by NMR analysis). The NMR spectrum of fraction 2 matched that of the neutral material isolated above from the attempted Michael condensation.

Acknowledgment. We thank Professor Keith Howard for discussion of this material.

Registry No. **1a**, 34456-05-8; **2a**, 92078-62-1; **2b**, 92078-60-9; **3**, 92078-63-2; **5**, 40967-67-7; dimethyl malonate, 108-59-8; chloroform, 67-66-3; methyl bromoacetate, 96-32-2; tetrabutylammonium hydroxide, 2052-49-5; tetramethyl 1,2,2,3-propanetetracarboxylate, 53046-85-8.

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[20] Bateman, L.; Jeffery, G. A. *J. Chem. Soc.* **1945**, 211. See also: Bateman, L.; Koch, H. P. *J. Chem. Soc.* **1945**, 216.

[21] Lit. mp 34.5 °C; see Bischoff, C. A. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 966.

A Straightforward Synthesis of (2*R*)-4-(Benzyloxy)-2-methyl-1-butanol from (*S*)-Citronellol

Kenji Uneyama, Hiroyuki Matsuda, and Sigeru Torii*

Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama 700, Japan

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Dolichol (**1**), a natural polyisoprenol, controls a glycoprotein synthesis important for maintaining the lives of organisms.[1] A practical and promising synthesis of **1** would be by coupling the naturally occurring polyisoprenol **2** with a Grignard reagent from a chiral C_5 unit **3b** (Scheme I).[2] An important problem to be solved for the manu-

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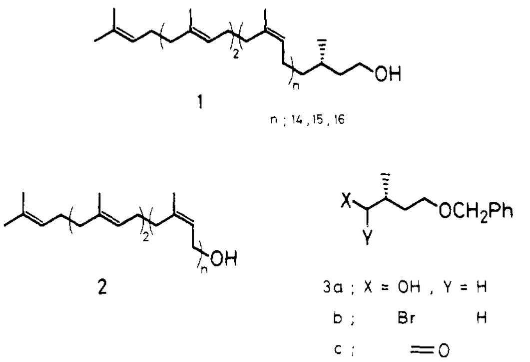
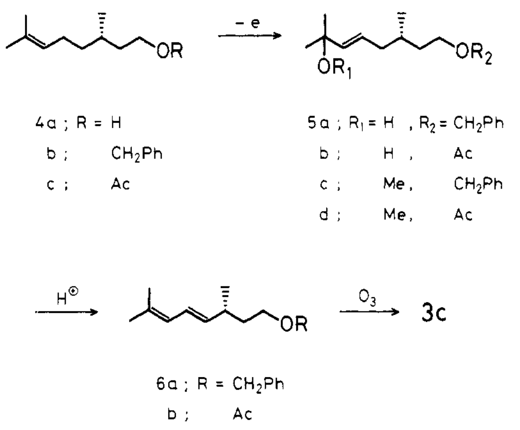
Scheme I



Scheme II



facturing of **1** is how to supply the optically active **3a** in a reasonable way. (3*R*)-3-Methyl-γ-butyrolactone and (2*S*)-2-methyl-γ-butyrolactone are possible precursors of **3a**. The former lactone has been prepared by a multistep asymmetric synthesis[3] and an optical resolution.[4] The latter lactone can be obtained by an enzymatic transformation of 4-hydroxy-2-methylbut-2-en-1-al ethylene acetal,[5] an asymmetric synthesis,[6] and an optical resolution from its *dl* form.[7] However, these conventional methods are not feasible for a large-scale production of **3a**. As part of our research program on the conversion of readily available natural products to chiral synthetic building blocks, we have devised a straightforward method for the preparation of (2*R*)-4-(benzyloxy)-2-methyl-1-butanol (**3a**) from (*S*)-citronellol (**4a**) by an electrochemical oxyselenation–deselenation sequence as a key step (Scheme II).

The electrochemical oxyselenation–deselenation of olefins is a useful method for the transformation of a carbon–carbon double bond to an alloxy moiety.[8] Thus, benzyl ether **4b** and acetate **4c** of (*S*)-citronellol ($[\alpha]^{20}_{D}$ −3.82°, c = 7.81, EtOH, 93.8% ee) were subjected to the selenium-mediated electrooxidation. In aqueous acetonitrile, the corresponding allylic alcohols **5a** and **5b** were obtained in 94% and 95% yields, respectively, by the use of a stoichiometric amount of diphenyl diselenide. On decreasing the amount of the diselenide, both the current efficiency and the yield are as follows: [percent of **5a** with $(PhSe)_2$, Et_4NBr, $MgSO_4$ (equiv relative to **4b**), and F/mol: 94% (0.5, 0.03, 0, and 7.6), 85% (0.25, 0.02, 0, and 5.5), 85% (0.13, 0.01, 0, and 3.9), 66% (0.06, 0, 2.1, and 3.0)]. In methanol, the use of 20 mol % of diphenyl diselenide afforded the corresponding methoxy compounds **5c** and **5d** in yields of 85% and 83%, respectively.

Acid-catalyzed demethoxylation or dehydration followed by isomerization of **5** were performed by the action of perchloric and sulfuric acids and boron trifluoride etherate. The dehydration of **5a** in THF proceeded even at room temperature within several minutes, affording a mixture of the 4,6- and 5,7-dienes. The 5,7-diene isomerized into the 4,6-diene **6a** under the reaction conditions slowly at room temperature but within several hours at 60–65 °C [**5a** → **6a**: 89% (60% $HClO_4$), 89% (BF_3 etherate), 81% (60% H_2SO_4); **5c** → **6a**: 91% (60% $HClO_4$)]. The reaction of acetates **5b** and **5d** proceeded more slowly than the benzyl ethers, being accompanied by partial hydrolysis of the ester, affording **6b**[9] in 72% yield. The diene **6a** was a mixture of the geometric isomers (4-*trans*:4-*cis* = 87:13 by ^1H NMR and HPLC).

The electrogenerated acid-catalyzed[10] dehydration of **5a** also resulted in a mixture of the 4,6- and 5,7-dienes (98%, 4,6-diene:5,7-diene = 40:60) in THF at room temperature (0.08 F/mol). However, isomerization of the 5,7-diene into **6a** under the electrolytic conditions was unsatisfactory.

Ozonolysis of **6a** in ether at −60 °C followed by reduction with zinc in methanol–acetic acid provided the aldehyde **3c**, which was subsequently reduced with sodium borohydride in ethanol, affording **3a** in 92% yield from **6a** ($[\alpha]^{18}_{D}$ +9.39°, c = 6.02, EtOH, 93% ee).[11] Therefore, (*S*)-citronellol benzyl ether (**4a**) was transformed into **3a** in 74% yield with a total retention of its asymmetric center.

Experimental Section

The ^1H NMR spectra were measured with Me_4Si as an internal standard by JEOL FX-100 (in $CDCl_3$) or Hitachi R-24 (in CCl_4) spectrometers. The IR spectra were recorded with a JASCO IRA-1 spectrometer. Optical rotations were taken on a JASCO DIP-140 digital polarimeter. The boiling points are indicated by an air-bath temperature without correction. Elemental analyses were performed in our laboratory.

(6*S*)-8-(Benzyloxy)-2,6-dimethyloct-3-en-2-ol (5a). A typical electrolysis procedure is as follows. A mixture of **4b** (100 mg, 0.41 mmol), $(PhSe)_2$ (63 mg, 0.20 mmol), and Et_4NBr (3 mg, 0.014 mmol) in MeCN (8 mL)–H_2O (2 mL) was electrolyzed at room temperature in a beaker-type undivided cell (3 cm in diameter and 10 cm in height) settled with two platinum foils as electrodes (2 × 1.5 cm^2). A constant current density (10 mA/cm^2) was supplied until 7.6 F/mol of electricity was passed by using Metronix DC power supply Model 543B. After concentration under reduced pressure, the residue was extracted with AcOEt and the organic layer was washed with saturated $NaHCO_3$ and brine and dried (Na_2SO_4). Evaporation of solvent and chromatography (SiO_2) provided **5a** as a colorless oil (98 mg, 94%): bp 83–86 °C (0.06 mmHg); $[\alpha]^{22}_{D}$ −3.16° (c 7.57, EtOH); ^1H NMR (CCl_4) δ 0.85 (d, J = 5 Hz, 3 H, CH_3), 1.20 (s, 6 H, CH_3), 1.30–2.10 (m, 5 H, CH_2, CH), 2.50 (br s, 1 H, OH), 3.40 (t, J = 6 Hz, 2 H, CH_2O),

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(11) The optical rotation of the optical pure **3a** is $[\alpha]^{24}_{D}$ +10.1° (c 4.0, EtOH). We are grateful to Dr. T. Takigawa, Central Research Laboratory, Kuraray Co. Ltd., Kurashiki, Japan, for informing us the $[\alpha]_D$ value of the optical pure **3a** prior to the publication.

4.35 (s, 2 H, CH_2Ph), 5.4–5.6 (m, 2 H, CH=), 7.15 (s, 5 H, Ph); IR (neat) 3400 (OH), 2960, 2920, 2860, 1455, 1370, 1100, 975, 740, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.66; H, 9.74. In a similar manner, **5b**[8] was obtained in 95% yield.

(3*S*)-7-Methoxy-3,7-dimethyloct-5-enyl benzyl ether (5c): bp 78–80 °C (0.025 mmHg); $[\alpha]^{24}_D$ −2.57° (*c* 1.44, EtOH); ^1H NMR (CCl_4) δ 0.90 (d, *J* = 5 Hz, 3 H, CH_3), 1.15 (s, 6 H, CH_3), 1.3–2.2 (m, 5 H, CH_2, CH), 3.02 (s, 3 H, CH_3O), 3.42 (t, *J* = 6 Hz, 2 H, CH_2O), 4.40 (s, 2 H, CH_2Ph), 5.3–5.6 (m, 2 H, CH=), 7.20 (br s, 5 H, Ph); IR (neat) 2965, 2920, 2860, 1450, 1375, 1360, 1100, 1075, 730, 690 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.38; H, 10.28. In a similar manner, **5d**[8] was obtained in 84% yield.

(3*S*)-3,7-Dimethyl-4,6-octadienyl Benzyl Ether (6a). To a solution of **5a** (500 mg, 1.9 mmol) in THF (16 mL) was added 60% $HClO_4$ aqueous solution (1.6 mL, 14.3 mmol) and the mixture was stirred for 1 h at 60–65 °C. After addition of water, the reaction mixture was extracted with ether and the organic layer was worked up in the usual manner to give **6a** as a colorless oil (445 mg, 89%): bp 74–76 °C (0.05 mmHg); $[\alpha]^{20}_D$ −49.60° (*c* 8.45, EtOH); ^1H NMR ($CDCl_3$) δ 1.02 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.50–1.65 (m, 2 H, CH_2), 1.76 (s, 6 H, CH_3), 2.10–2.60 (m, 1 H, CH), 3.52 (t, *J* = 6.6 Hz, 2 H, CH_2O), 4.45 (s, 2 H, CH_2Ph), 5.46 (dd, J_1 = 14.8 Hz, J_2 = 7.6 Hz, 1 H, CH=), 5.82 (d, *J* = 10.7 Hz, 1 H, CH=), 6.26 (dd, J_1 = 14.8 Hz, J_2 = 10.7 Hz, 1 H, CH=), 7.40 (s, 5 H, Ph); IR (neat) 2960, 2920, 2860, 1660, 1455, 1365, 1100, 730, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O$: C, 83.61; H, 9.83. Found: C, 83.36; H, 9.80. The reaction of **5b** and **5d** in the similar conditions provided **6b**[9] in 72% yield.

Electrochemical Dehydration of 5a. A mixture of **4b** (60 mg, 0.24 mmol) and $LiClO_4$ (125 mg, 1.18 mmol) in dry THF (8 mL) was electrolyzed at room temperature under a constant current (3.3 mA/cm^2 for 3 min, 0.08 F/mol) using platinum foils as electrodes in a breaker-type undivided cell. After addition of saturated $NaHCO_3$ and evaporation of solvents under reduced pressure, the usual workup and chromatography (SiO_2) provided **6a** as a regioisomeric mixture (59 mg, 98%; 4,6-diene:5,7-diene = 40:60 by VPC).

(2*R*)-4-(Benzyloxy)-2-methyl-1-butanal (3c). Ozonolysis was carried out by bubbling ozone through the ether (50 mL) solution of **6a** (500 mg, 2.05 mmol) at −50 to −60 °C for 8 h. After bubbling N_2 gas for 20 min, water (5 mL) and AcOH (1.5 mL) were added to the mixture to which was added zinc powder (100 mg) and AcOH (1 mL). Under vigorous stirring at room temperature for 15 min, another 100 mg of zinc and AcOH (1 mL) were added and the stirring was continued for 10 min. This procedure was repeated 5 times in every 10 min. After final addition of zinc (200 mg), the mixture was stirred at room temperature for 3 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. The usual workup of the residual mixture gave the crude aldehyde which was reduced with $NaBH_4$ without further purification. An analytical sample of **3c** was obtained by chromatography and distillation: bp 73–75 °C (0.025 mmHg); $[\alpha]^{24}_D$ −11.61° (*c* 3.28, hexane); ^1H NMR (CCl_4) δ 1.00 (d, *J* = 7 Hz, 3 H, CH_3), 1.25–2.10 (m, 2 H, CH_2), 2.10–2.60 (m, 1 H, CH), 3.38 (t, *J* = 6 Hz, 2 H, CH_2O), 4.33 (s, 2 H, CH_2Ph), 7.12 (s, 5 H, Ph), 9.40 (d, *J* = 2 Hz, 1 H, CHO); IR (neat) 3020, 2920, 2860, 2710, 1725 (C=O), 1455, 1370, 1100, 740, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.16; H, 8.25.

(2*R*)-4-(Benzyloxy)-2-methyl-1-butanol (3a). A solution of **3c** (250 mg, 1.3 mmol) in EtOH (5 mL) was added dropwise to a solution of $NaBH_4$ (49 mg, 1.3 mmol) in EtOH (5 mL) in an ice bath and the mixture was stirred for 1 h at room temperature. The usual workup and chromatography (SiO_2) provided **3a** as a colorless oil (230 mg, 92% from **6a**): bp 68–70 °C (0.03 mmHg); $[\alpha]^{18}_D$ +9.39° (*c* 6.02, EtOH); ^1H NMR ($CDCl_3$) δ 0.94 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.4–2.0 (m, 3 H, CH_2, CH), 2.6 (br s, 1 H, OH), 3.3–3.7 (m, 4 H, CH_2O), 4.56 (s, 2 H, CH_2Ph), 7.23 (s, 5 H, Ph); IR (neat) 3360 (OH), 2920, 2860, 1455, 1365, 1100, 1040, 740, 695 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.10; H, 9.19.

Registry No. **1** (*n* = 14), 89363-37-1; **1** (*n* = 15), 89363-38-2; **1** (*n* = 16), 89363-39-3; **3a**, 73408-07-8; **3c**, 91550-14-0; **4a**, 7540-51-4; **4b**, 84237-05-8; **4c**, 67601-05-2; **5a**, 92142-15-9; **5b**, 90359-34-5; **5c**, 92078-51-8; **5d**, 92056-72-9; (*E*)-**6a**, 92056-73-0; (*Z*)-**6a**, 92056-74-1; **6b**, 92142-16-0; (3*S*)-3,7-dimethyl-5,7-octadienyl benzyl ether, 92056-75-2.

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^{17}O NMR Spectroscopic Study of Substituted Benzoyl Cations[1]

George A. Olah,* Pradeep S. Iyer, G. K. Surya Prakash, and V. V. Krishnamurthy

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

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The structure of benzoyl and acylium cations has been well studied in our laboratory as well as others by a variety of methods.[2] Ample evidence suggests that the benzoyl cations **1** may be adequately described in terms of resonance hybrids shown in Scheme I with a substantial contribution from the "ketene-like" mesomer **1C**.

On the other hand, the acylium ion structure **2** is predominantly dominated by the contributions from resonance hybrids of the oxocarbenium ion **2A** and the oxonium ion **2B**. Such interpretations were further reinforced during our recent study of one-bond ^{13}C–^{13}C coupling constants in a series of substituted benzoyl cations.[3] Interested in probing the substituent-induced electronic effects at the terminal oxygen center of carbocationic carbonyl moiety, we analysed these systems by ^{17}O NMR spectroscopy.

Results and Discussion

The ^{17}O NMR chemical shifts of all the substituted benzoyl cations were measured in natural abundance samples (~0.037%) and are listed in Table I. A remarkably constant value around 320 ppm is obtained for the cationic carbonyl oxyen with the entire range of substituents (i.e., from the most electron donating 4-OCH_3 to the most electron withdrawing 4-CF_3).

We have previously reported the δ ^{17}O of acetyl and propionyl cations to be ~300 ppm.[4] Since the acyl cations may be primarily described by the resonance hybrid of mesomers **2A** and **2B** (Scheme I), the ~20 ppm relative deshielding observed in the benzoyl cations **1** may well reflect the greater contribution from the "ketene-like" mesomer **1C**. A closer look at the mesomers **1A** and **1B** (Scheme I), however, shows that a simple qualitative analysis of ^{17}O may not be easy, since the oxygen atom changes its hydridisation from sp^2 to sp, respectively. Since an sp-hybridized oxygen has a chemical shift value ($\delta^{17}O$ of model carbon monoxide being 350)[5] intermediate to a sp^2 (δ ^{17}O 600) and sp^3 ($\delta^{17}O$ 0–50) hybridized oxygen, a triple bond may be assumed to cause a diamagnetic

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